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Our research efforts have been focused on the magnetic hardening behavior of R-Fe-B magnets, the development of processing techniques for improved magnetic properties and the search for new phases with better magnetic properties. The origin of magnetic hardening was examined by correlating the microstructure, microchemistry and magnetic domain structure with the magnetic properties. This was done on powders, ribbons and sintered magnets where the effects of Co, Al and Dy were examined. High coercivities have been obtained in as-cast Nd(Pr)Fe-B alloys with impurity additions (Cu,Al,Ga,Ag) indicating the potential of these materials for hot extruded magnets. New anisotropic magnetic phases have been found in Nd-Fe-O alloys and in rare-earth carbides. Both of these systems have the potential for permanent magnet development.

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3. "The Effect of Al Substitutions on the Coercivity of Nd-Fe-B Magnets," J. Strzeszewski, G. C. Hadjipanayis and A. S. Kim, J. Appl. Phys. 64, 5568 (1988).

4. "Effect of Heat Treatment on Magnetic Hysteresis in Nd-Fe-B Based Magnets," J. Strzeszewski, G. C. Hadjipanayis and A. Kim, J. de Physique C8, 1633 (1988).

5. "High Coercivities in As-Cast Pr-Fe-B and Nd-Fe-B Alloys with Impurity Additions," G. C. Hadjipanayis, M. Zhang and C. Gao, Appl. Phys. Lett. 54, 1812 (1989).

6. "A New Hard Magnetic Phase in Binary Nd-Fe and Pr-Fe Alloys," G. C. Hadjipanayis, A. Tsoukatos, J. Streszewski, G. J. Long and D. A. Pringle, J. Magn. Magn. Mat. L1, 78 (1989).

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RESEARCH FINDINGS

Our research has been focused on three different areas,

(i) Search for new phases or compounds that can be used for permanent magnet development,

(ii) New processing techniques to reduce the manufacturing cost of high performance permanent magnets,

(iii) Magnetic hardening studies in sintered Nd-Fe-B based magnets.

A. New Phases

1. <u>Nd(Pr)-Fe-Oxides</u>

Recent studies have shown that oxygen might lead to stable ternary R-Fe-O phases which may be anisotropic. In our studies for new magnetic phases and special microstructures we have recently obtained high coercivities in as-cast Nd-rich Nd-Fe alloys corresponding to a phase with a T_C around 270 K. We first associated this phase with $NdFe_2$ without excluding the possibility of an oxygen stabilized Nd-Fe-O phase. However, after additional magnetic and structural studies we believe that this phase is not $NdFe_2$, but rather a new phase stabilized with oxygen.

The new magnetic phase has been observed in as-cast and melt-spun Nd-Fe and Pr-Fe alloys with a Curie temperature around 265°C. SEM studies show the presence of this phase in the form of spherical and elongated particles 5 μm in size with a composition having a ratio of Fe/Nd = 4:1. This phase is believed to be a ternary Nd-Fe-O phase stabilized with oxygen. The phase appears to have a high anisotropy leading to coercivities of about 6 kOe in as-cast samples at room temperature. The Mössbauer spectra of this phase can be fitted to four Fe sites with magnetic moments ranging from 1.7 to 2.54 μ_B.

2. R-Fe-Carbides

In previous studies we have shown that carbon can be substituted for much of the boron in R-Fe-B alloys and the 2:14:1 phase can still be formed. At that time it was reported that 75% of boron can be substituted with carbon in alloys containing neodymium and praseodymium. The anisotropy field and saturation magnetization were found to decrease substantially with carbon addition. In Dy-Fe-C the 2:14:1 phase was found to be formed with carbon and a high coercivity was observed in as-cast samples.

Recently we have prepared melt-spun R-Fe-C alloys and we studied their magnetic properties. The highest coercivities were obtained in melt-spun $Nd_{14}Fe_{80}C_6$ and $Pr_{14}Fe_{80}C_6$ samples which were heat treated at 750°C for 2-15 min. The Curie temperature of the $(Nd,Pr)_2Fe_{14}C$ phase was approximately 290°C.

The high coercivities are attributed to a fine grain microstructure (grain size, 800 Å) which is formed during crystallization. The same behavior has been observed in melt-spun Nd(Pr)-Fe-B alloys. The $(Nd,Pr)_2Fe_{14}C$ phase is believed to be present in as-cast alloys too. However, the phase is formed at low temperatures (below 900°C) and therefore very long annealing times are needed to obtain a single-phase sample. We are presently trying to produce single-phase $(Nd,Pr)_2Fe_{14}C$ as-cast alloys in an attempt to study their intrinsic magnetic properties.

B. **High Coercivity in As-cast Nd-Fe-B Based Alloys**

As-cast $R_{17}Dy_xFe_{77}B_yM_{1.5}$ alloys with R = Pr, Nd, M = Al, Cu, Fe, Ag, and x = 0, 1.5, y = 3, 5 were made by arc melting. The high coercivities were obtained after a homogenization heat treatment in the temperature range of 900-1100°C. In some samples it was found that further annealing at a lower temperature (600-750°C) leads to a substantial increase in coercivity. The magnetic properties were measured with a vibrating sample magnetometer. The microstructure and chemical composition of the sample's surface was obtained with a scanning transmission electron microscope equipped with an energy dispersive x-ray detector.

The samples are isotropic with a random distribution of grains showing an initial magnetization curve characteristic of melt-spun ribbons. It is interesting to note that now high coercivities can also be obtained in as-cast Nd-Fe-B(M) samples and in samples with other substitutions M beside Cu. In the Nd-Fe-B(M) samples the highest coercivities (~ 6 kOe) have been obtained in Ag-substituted samples. In as-cast Pr-Fe-B(M) alloys the highest coercivities have been obtained in Cu- and Al-substituted samples. Additions of small amounts of Dy lead to an increase in coercivity in Nd-Fe-B(M), but to a decrease in H_c in Pr-Fe-B(M). The reason for this is not yet well understood.

For most of the samples the highest H_c are obtained after an overnight heat treatment at 900°C. In some samples the coercivity can be further increased after an additional annealing heat treatment at a lower temperature. The coercivity is increased by about 4 kOe after annealing.

Thermomagnetic data [$M_H(T)$] show the presence of two magnetic phases with Curie temperatures 320 and 80°C, respectively. The phase with the higher Curie temperature is believed to be $R_2Fe_{14}B$. The lower Curie temperature phase is identified at R_2Fe_{17}. In some samples, the amount of R_2Fe_{17} is increased after the M vs T experiment, where the temperature was increased to 400°C.

Microstructural studies showed the presence of three phases consistent with the thermomagnetic data. The majority phase is $R_2Fe_{14}B$ while the minority phase is R and Cu-rich. The other phase is R_2Fe_{17}. The R-Cu-rich phase is observed at the grain boundaries of the $R_2Fe_{14}B$ phase and is uniformly distributed throughout the sample. This type of microstructure is characteristic of sintered Nd-Fe-B magnets. In the latter magnets an oxygen-stabilized Nd-Fe-O hard magnetic phase is believed to exist in the Nd-rich phase causing domain wall pinning at grain boundaries. A similar phase may exist in the magnets of this study. The addition of impurities appears to promote the formation of this phase which is uniformly distributed at grain boundaries after a homogenization heat treatment.

C. Magnetic Hardening Studies

We have investigated the effect of Al and post-sintering heat treatment on the hard magnetic properties of Nd-Fe-B based magnets.

1. Effect of Al Substitutions

The effect of Al on the coercivity of Nd-Dy-Fe(Al)B magnets has been investigated with magnetic measurements, differential scanning calorimetry, and microstructure studies. The Al containing samples were found to have a much higher coercivity, a relatively steeper initial magnetization, a different $H_C(H_{ef})$ curve, and a larger temperature coefficient of coercivity than the samples without Al. Morphology studies made with a scanning transmission electron microscope did not show any significant differences between the two samples. The only evident difference, found in x-ray and electron diffraction data, was in the c/a ratio of the $Nd_2Fe_{14}B$ tetragonal phase which was higher for the sample with Al. Another difference was observed in the magnetization reversal mechanism. In the Al-containing samples the magnetization is reversed by changing the magnetization of entire grains, while for the samples without Al the magnetization is reversed by dividing into domains inside the grains.

2. Effect of Heat-Treatment

Studies of the differently heat-treated magnets performed with scanning electron microscopy on fractured and polished samples, revealed a morphology consisting of the majority 2:14:1 phase grains (~ 8-15 μm) and smaller grains of minority B-rich and Nd-rich phases. The biggest difference in morphology between the different kind of samples was in the shape of grains of $Nd_2Fe_{14}B$ phase. The shape of the grains after sintering is irregular with a lot of sharp edges, corners, and concave surfaces. The post-sintering and subsequent annealing processes change the grain shapes to more regular polyhydra having flat surfaces and less sharp edges and corners. In our opinion the irregular shapes, sharp edges or corners might be the places of higher demagnetizing fields and therefore easier nucleation or unpinning of domain walls.

Transmission electron microscope studies show a rather perfect crystal structure of the main phase for all samples. Interactions between domain walls in the main phase and the spherulites of Nd-rich phase were observed. However, we do not think that this interaction is strong enough to explain the high coercivity.

We think that the changes of coercivity which occur after heat-treatment are related to macroscopic changes of the grain morphology rather than microscopic changes at around grain boundaries.